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(54) Title: COMPRESSIBLE PREFORM INSULATING LINER (57) Abstract <p>The invention provides a preform insulating end cone (30, 60) suitable for forming the end cone of a pollution control device (10), said preform (30, 60) comprising a cone shaped intumescent or non-intumescent sheet material (40) with or without a plurality of splits (49) enabling said sheet material (40) to be cone shaped and a shape retaining element in intimate contact with said intumescent sheet material (40), said shape retaining elements enabling said intumescent sheet material (40) to maintain a cone shape. The invention also provides methods of making preform insulating end cones (30, 60) of the invention.</p> <div data-bbox="714 1155 1323 1722"> </div>		

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COMPRESSIBLE PREFORM INSULATING LINER

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Background of the Invention

The present invention relates to insulating materials used in pollution control devices and more particularly to a method for making a preform from an intumescent or a non-intumescent sheet material for use as an insulating end cone
10 in pollution control devices and the resulting preform insulating end cones.

Two types of pollution control devices are currently in wide spread use — catalytic converters and diesel particulate filters or traps. Catalytic converters contain a catalyst, which is typically coated on a monolithic structure mounted in the converter. Monolithic structures are typically ceramic, although metal monoliths
15 have been used. The catalyst oxidizes carbon monoxide and hydrocarbons, and reduces the oxides of nitrogen in automobile exhaust gases to control atmospheric pollution. Diesel particulate filters or traps are wall-flow filters which have honeycombed monolithic structures typically made from porous crystalline ceramic materials. Alternate cells of the honeycombed structure are typically plugged such
20 that exhaust gas enters one cell and is forced through the porous wall of one cell and exits the structure through another cell.

Due to the relatively high temperatures encountered in pollution control devices, it is important that the device be well insulated. Insulation is typically provided by securely mounting the monolithic element within the casing using an
25 insulating mounting mat comprised of a suitable material. In addition, inlet and outlet end cone assemblies which provide a transition from the exhaust pipe to the pollution control device can also be insulated. The inlet and outlet end cone assemblies can be insulated by providing a double-walled end cone assembly comprising an outer metal housing and an inner metal housing, with a gap defined
30 between the inner and outer cone housings.

Summary of the Invention

One aspect of the invention is a preform insulating end cone suitable for forming the end cone of a pollution control device, said preform comprising a cone shaped intumescent or non-intumescent sheet material having a plurality of slits
5 enabling said sheet material to be cone shaped and a shape retaining element in intimate contact with said intumescent sheet material, said shape retaining element enabling said intumescent sheet material to maintain a cone shape.

Another aspect of the invention is a preform insulating end cone suitable for forming the end cone of a pollution control device, said preform comprising a
10 cone shaped intumescent sheet material having a first end and a second end, and a shape retaining element in intimate contact with said intumescent sheet material, said shape retaining element enabling said intumescent sheet material to maintain a cone shape. Preferably, said shape retaining element in this embodiment is a tape joining said ends together. Preferably, the sheet material is coated on one side that
15 the tape is adhered to with a thermoplastic polymer film such as polyester, polyethylene, or polypropylene.

The invention also provides a method of making a preform insulating end cone for use as an insulating material in an end cone assembly in a pollution control device from a sheet material. In one aspect, the invention provides a
20 method of making a preform insulating end cone comprising the steps of forming an intumescent or non-intumescent sheet material containing a thermoplastic organic binder and cut to the desired shape and dimensions to form a finished preform insulating end cone, treating the formed sheet material with water or steam, and then drying the treated sheet material to form the finished preform
25 insulating end cone. Preferably, the cut sheet material is formed by means of a mold. Preferably, the cut sheet material has a plurality of V-shaped cuts. Preferably, the sheet material is intumescent and contains a thermoplastic organic binder derived from a latex.

In another aspect, the invention provides a method of making a preform
30 insulating end core comprising the steps of treating at least one surface of a flexible and resilient intumescent or non-intumescent sheet material with a rigidizing solution, said sheet material being suitable for use in pollution control devices and

cut to a desired size and shape to form a finished preform insulating end cone, forming the sheet material into the desired end cone shape, and then drying the sheet material to form the finished preform insulating end cone. Preferred rigidizing solutions are aqueous colloidal silica and aqueous colloidal alumina.

- 5 Preferred intumescent and non-intumescent sheet materials contain an organic binder comprising a polymer emulsion.

In another aspect, the invention provides a method of making a preform insulating end cone comprising the steps of providing a flexible and resilient intumescent or non-intumescent sheet material suitable for use in a pollution
10 control device, coating at least one side of the sheet material with a metal foil and then forming the coated sheet material to the desired shape to form the finished preform end cone insulating material. Preferably, the metal foil is a metal foil tape that is laminated to at least one surface of the intumescent or non-intumescent sheet material before the sheet material is cut to the desired dimensions. The metal foil
15 can also be laminated to both sides of the sheet material.

In another aspect, the invention provides a method of forming a preform insulating end cone comprising the steps of providing a flexible and resilient intumescent or a non-intumescent sheet material cut to the desired dimensions and initially formed into the desired shape, partially wrapping the formed material with
20 a heat shrinking film, and then exposing the heat shrinking film wrapping to sufficient heat to form the finished preform.

Surprisingly, Applicants have discovered simple and less time consuming methods of forming preform insulating end cones from insulating materials in sheet form without the need for preparing and handling dilute slurries of inorganic
25 materials. The resulting preforms of the methods of the invention are flexible and self supporting and are thus easy to use in the manufacture of pollution control devices.

One of the advantages of the preforms of the invention is that the preforms of the invention remain relatively flexible, resilient, and compressible and
30 maintain the chemical and performance characteristics of the sheet material used to make the preform.

As used herein, "self supporting" refers to a formed article which maintains a three dimensional shape under the force of gravity after having been formed.

As used herein, a "preform" end cone insulating material means a self-supporting insulating end cone made from an intumescent or a non-intumescent
5 sheet material.

As used herein, an "intumescent" material means a material suitable for use in a pollution control device that contains an intumescent material and swells or intumesces when exposed to sufficient thermal energy.

As used herein, a "non-intumescent" material is a material that is suitable
10 for use in a pollution control device that does not contain an intumescent material.

Brief Description of the Drawings

Figure 1 shows a cross sectional view of a catalytic converter having inner and outer metallic end cone housings with a preform insulating end cone disposed
15 between the end cone housings.

Figure 2 shows a die cut sheet material prior to being treated.

Figure 3 shows a perspective view of a preform insulating end cone of the invention made from the die cut material shown in Figure 2.

Figure 4 shows a die cut sheet material prior to being treated.

Figure 5 shows a perspective view of a preform insulating end cone of the invention made from the die cut sheet material shown in Figure 4.
20

Figure 6 shows view of another embodiment of the preform end cone of the invention.

Figure 7 shows a front view of another embodiment of the preform end
25 cone of the invention.

Detailed Description of the Invention

Referring now to the Figures, Figure 1 shows a pollution control device, and in particular, a catalytic converter 10 which comprises a housing 12 with generally
30 conical inlet end cone assembly 14 and outlet end cone assembly 16. The housing 12, which is also referred to as a can or a casing, can be made from suitable materials known in the art, and is typically made of metal. Preferably, the housing 12 is made

of stainless steel. Disposed within housing 12 is a monolithic catalytic element 18 formed of a honeycombed monolithic body either of ceramic or metal. Surrounding monolith 18 is a mounting and insulating mat 22.

Referring now to inlet end cone assembly 14 and outlet end cone assembly 16, it can be seen that inlet end cone assembly 14 and outlet end cone assembly 16 each comprise an outer end cone housing 26 and an inner end cone housing 28. A preform insulating liner or end cone 30, shown more particularly in Figure 3, is positioned between outer end cone housing 28 and inner end cone housing 26. Inner end cone housing 28, is provided in pollution control devices to retain insulating end cone 30 in position and to prevent insulating end cone 30 from being damaged by hot exhaust gases passing through the pollution control device. Inner and outer end cone housings 26, 28 are typically made of metal and are preferably made from stainless steel or an alloy such as INCONEL™ 600.

Figure 2 shows an embodiment of an insulating material 40 that has been die cut from an intumescent sheet material suitable for use in pollution control devices. Die cut insulating material 40 is one piece and has dimensions and shape such that it can be disposed between inner and outer end cone housings 28, 26. Die cut insulating material 40 is generally in the form of a sheet having major surfaces 42, 44 and a thickness 46. In this embodiment, die cut insulating material 40 has generally "V-shaped" cuts 48 forming tabs 50. The V-shaped cuts 48 relieve the surface tension of the sheet material and allow the die cut material 40 to be formed into a generally conical shaped insulating material without excessive buckling or folding of the insulating material. The shape and size of V-shaped cuts 48 in the die cut material are such that gaps in the insulating material are minimized without undesirable buckling or folding of the material when the die cut material 40 is formed into the final desired shape. Of course, the insulating sheet material may be cut into any useful or desired single piece shape capable of being formed into a cone shape with dimensions suitable for the end use. A useful die cutting machine for intumescent and non-intumescent sheet materials is a Rotomatic™ II die cutter commercially available from Ampak, Inc., Anderson NC.

One embodiment of a preform insulating end cone of the invention is shown in Figure 3 as preform insulating end cone 60. Preform insulating end cone 60 is a

finished end cone made from die cut material 40 shown in Figure 2. Preform insulating end cone 60 is characterized as being three dimensional, cone shaped and having a front 62 and a back 64 and is self-supporting yet resilient and compressible. When die cut sheet material 40 is formed into preform 60, V-shaped cuts 48 become
5 slits 49. In this embodiment, the sheet material is INTERAM™ Type 200 intumescent mat (3100 g/m^2) major surface 44 has been treated and formed using a shape retaining element in the form of a rigidizing solution containing colloidal silica.

Figure 4 shows a die cut sheet material 70 that is used to make a preferred
10 preform insulating end cone 80 shown in Figure 5. Referring to Figure 4, die cut sheet material 70 is one piece and generally half-moon shaped and has a first end 72 and second end 74 which are attached together by a shape retaining element in the form of a tape 82 to form preform insulating end cone 80 (Figure 5). Preform insulating end cone 80 is characterized as being self-supporting in a cone shape and
15 is resilient and compressible. In this preferred embodiment, die cut sheet material 70 is cut from is INTERAM™ Type 100 intumescent mat (3662 g/m^2) that has been laminated with a thermoplastic polyester film 76 on one surface before being die cut. Useful thermoplastic films for laminating to the surface of intumescent sheet materials include polyester, polyethylene and polypropylene having a thickness of
20 from about 0.01 mm to about 0.3 mm. A preferred commercially available film is 3M Tape # 356, from Minnesota Mining and Manufacturing Company, St. Paul, MN. Any tape that will adhere sufficiently to substantially inorganic intumescent or non-intumescent sheet materials and/or to thermoplastic films used for lamination to the sheet material can be used as the shape retaining element for this embodiment. Such
25 useful tapes include masking tapes, cloth tapes, surgical tapes, and plastic film tapes such as a polyester film tape, commercially available as 3M Tape # 356, from Minnesota Mining and Manufacturing Company. A preform insulating end cone is made by bringing the ends 72, 74 together to form a cone and then attaching the ends together with adhesive tape.

30 Another embodiment of a preform insulating end cone is shown in Figure 6 as preform insulating end cone 90. End cone 90 comprises a cone shaped intumescent sheet material 91 in the shape of a cone having a plurality of slits 49 and

a shape retaining element in the form of a metal foil tape 92 laminated to inner or front surface 94.

Another embodiment of a preform insulating end cone of the invention is shown in Figure 7 as preform insulating end cone 100. End cone 100 comprises a cone shaped intumescent sheet material 91 in the shape of a cone having a plurality of slits 49 and a shape retaining element in the form of a heat shrinkable film 102 applied over a top portion of front surface 104 and back surface 106 of the cone shaped sheet material.

The die cut sheet materials used to form the cone shapes can be made from any flexible and resilient insulating sheet material suitable for use in pollution control devices. The material can be intumescent or non-intumescent and is preferably intumescent.

A useful intumescent sheet material for making die cut insulating material 40, 60 comprises a resilient, flexible intumescent sheet comprising from about 20 to 65 percent by dry weight of unexpanded vermiculite flakes, such flakes being either untreated or treated by being ion exchanged with ammonium compound such as ammonium dihydrogen phosphate, ammonium carbonate, ammonium chloride or other suitable ammonium compound as described in U.S. Patent No. 4,305,992 (Langer et al.); from about 10 percent to 50 percent by dry weight of inorganic fibrous material including aluminosilicate fibers (commercially available under the trademarks FIBERFRAX™ from Unifrax Co., Niagara Falls, NY, and CERA-FIBER™ from Thermal Ceramics, Augusta, GA), glass fibers, zirconia-silica, and crystalline alumina whiskers; from about 3 to 25 percent by dry weight of organic binder including those in latex form for example, natural rubber lattices, styrene-butadiene lattices, butadiene acrylonitrile lattices, lattices of acrylate or methacrylate polymers and copolymers and the like; and up to about 40 percent by dry weight of inorganic filler including expanded vermiculite, hollow glass microspheres and bentonite. A preferred intumescent sheet material comprises about 45 to about 62 dry weight percent unexpanded vermiculite flakes, about 27 to about 45 dry weight percent inorganic fibrous material, and about 3 to about 10 percent organic binder in latex form.

Examples of other useful sheet materials and methods of making the sheet materials include those described in U.S. Patent No. 5,523,059 (Langer).

Further, examples of intumescent sheet materials and methods of making such sheet materials include those described in U.S. Patent Nos. 3,916,057 (Hatch et al.), 4,305,992 (Langer et al.), 4,385,135 (Langer et al.), 5,254,410 (Langer et al.), 4,865,818 (Merry et al.), 5,151,253 (Merry et al.), and 5,290,522 (Rogers et al.). Preferred commercially available intumescent sheets and mats includes those sold under the INTERAMTM tradename by Minnesota Mining and Manufacturing Co. of St. Paul, MN. The intumescent sheet materials are made using well know
10 papermaking techniques. The mounting mats typically range in thickness from 0.5 to 10 mm.

Other useful intumescent materials include expandable graphite, expandable sodium silicate granules, and partially dehydrated vermiculite as described in U.S. Patent No. 5,254,410 (Langer et al.).

15 One example of a shape retaining element is an organic binder. Thermoplastic organic binders include emulsions of organic polymers and elastomers in latex form such as natural rubber lattices, styrene-butadiene lattices, butadiene acrylonitrile lattices, and lattices of acrylate and methacrylate polymers and copolymers. Thermoplastic organic binders also include polymers and polymer resins
20 such as natural rubber, styrene-butadiene rubber, and other elastomeric polymer resins. Acrylic latex and polyvinyl acetate are preferred thermoplastic organic binders. Other useful thermoplastic materials for use as organic binders include polypropylene, polyvinyl alcohol, polyvinyl chloride and polystyrene.

Useful thermosetting materials for use as organic binders include epoxies and
25 phenolics. The organic binder may also include mixtures of two or more thermoplastic and/or thermosetting materials. Useful mixtures include a polymer emulsion combined with a thermoplastic resin or material and a polymer emulsion combined with a thermosetting resin or material.

Examples of preferred commercially available organic binders include
30 RHOPLEX® HA-8 (a 45.5 percent by weight solids aqueous acrylic emulsion) from Rohm & Haas, Philadelphia, PA and AIRFLEX® 600BP (a 55 percent solids aqueous polyvinyl acetate emulsion) from Air Products, Allentown PA.

Inorganic fillers include expanded vermiculite, hollow glass microspheres, and bentonite.

Useful non-intumescent insulating sheet materials for forming the preform insulating end cones of the invention generally comprise inorganic fibers and organic binder. Generally, useful non-intumescent sheet materials comprise from about 60 to about 98 dry weight percent inorganic fiber and from about 2 to about 25 dry weight percent organic binder. A preferred non-intumescent sheet material comprises about 90 percent inorganic fiber and about 10 percent organic binder. The non-intumescent material may also contain inorganic particles or fillers and one or more inorganic binders. The non-intumescent insulating material is preferably in the form of a sheet having a thickness of from about 0.5 to about 15 mm.

Essentially shot-free ceramic fibers useful in forming non-intumescent insulating sheet materials include alumina-boria-silica fibers, alumina-silica fibers, alumina-phosphorus pentoxide fibers, zirconia-silica fibers, zirconia-alumina fibers, and alumina fibers. "Essentially shot free" or "shot free" fibers are fibers that contain less than 5 percent by weight and preferably less than 1 percent by weight of shot or non-fibrous particulate material and fibers which are at least 95 percent shot-free and preferably 99 percent shot-free. Useful commercially available fibers include those under the trademarks FIBERMAX™, available from Unifrax, SAFFIL™ LD, available from ICI Chemicals & Polymers, ALCENT™ alumina fibers available from Denka, and MAFTECH fibers, available from Mitsubishi.

The fibers are typically formed by blowing or spinning using methods known in the industry. Preferable, the fibers are formed by spinning a sol gel solution. The fibers are formed into a mat or sheet by various known methods including blowing the fibrous material onto a collection screen as is practiced in the nonwoven industry. A preferred non-intumescent inorganic fiber is a polycrystalline alumina fiber, available under the trademark SAFFIL™ from ICI Chemicals and Polymers. The fiber is chemically resistant and may be used in selected applications up to 1600°C. It is produced in a low density sheet form which consists of a predominately two-dimensional random orientation of fiber resulting in a mat of lamella form. The sheet is essentially shot-free with a uniform fiber structure.

The lamella nature of the low density mat makes it necessary to introduce the means for preventing delamination during handling and assembly in the pollution control device. That is, the low density sheet of alumina fiber is preferably physically restrained or compressed during handling and assembly. When compressed to a
5 mount density of about 0.05 and 0.60 grams per cubic centimeter these materials have a unique ability to repeatedly undergo a reduction in thickness while hot and spring back to substantially their original thickness when cooled, thus maintaining their structural integrity.

Since the fiber material preferred for the non-intumescent preform insulating
10 end cones 60 are generally available in the density range of 0.05 to 0.30 grams per cubic centimeter, they must be compressed by about a factor of 1 to 10 when used as insulating materials within the end cone housings 28, 26. Sheets of the non-intumescent insulating material are generally compressed and held in the compressed state to facilitate handling and cutting of the material. The non-intumescent insulating
15 sheet material may be physically compressed in a variety of manners, including the use of resin bonding, or needle punching.

Resin bonding is accomplished by saturating the non-intumescent material with organic binders which burn off in the presence of heat generated from hot exhaust gas. The organic materials burn off when exposed to heat generated from
20 hot exhaust gas.

Preferred commercially available non-intumescent sheet materials are SAFFIL™ LD alumina fiber sheet (from ICI Chemicals and Polymers, Cheshire, England) and FIBERFRAX™ 550K fiber sheet (from Unifrax, Niagara Falls, NY).

Organic binders and organic fibers that are useful in non-intumescent sheet
25 materials include those described above for intumescent sheet materials.

The intumescent and non-intumescent sheet materials that are useful for the present invention are made by well known wet laid methods including methods used to make paper.

One method of making the finished preforms of the invention from a flexible
30 and resilient intumescent or non-intumescent sheet material includes the step of treating at least one of the major surfaces of the intumescent or non-intumescent sheet material. The surface treatment is applied to at least one surface of the sheet

material to add enough rigidity to the material so that after the material is formed into the shape of an end cone, the preform end cone will be self-supporting but not be so rigid so to be prone to cracking or breaking during handling for its intended use.

Useful surface treatments include applying a shape retaining element in the form of a rigidizing solution to at least one surface of the sheet material. A rigidizing solution is a solution that when applied to the surface of a sheet material and then dried, stiffens or makes rigid the surface to which the solution was applied. The solutions may be applied to the surfaces of the intumescent or non-intumescent sheet material by means of a brush or a sprayer. Useful rigidizing solutions include saturated solutions of colloidal silica, colloidal alumina, silicon carbide, magnesium phosphate, vermiculite emulsions, clay emulsions, and monoaluminum phosphate.

Useful commercially available rigidizing solutions include a magnesium phosphate suspension (100% solids, from ZYP Coatings, Inc., Oak Ridge, TN), Nalco 2327 colloidal silica (50% solids, from Nalco Chemical Company, Naperville, IL), and a 50% solids solution of monoaluminum phosphate (Technical Grade, from Rhone-Poulenc Basic Chemical Co., France). Preferred rigidizing solutions are solutions of colloidal alumina and colloidal silica. Preferably, only one of the surfaces of the sheet material is treated with a rigidizing solution. In use, the treated surfaces of the preforms of the invention are adjacent to the outer surface of the inner end cone housing.

Generally, the amount of a rigidizing solution applied to the surface of the intumescent or non-intumescent sheet material can vary depending upon the desired characteristics of the end product. However, the treatment should be in a sufficient amount so as to provide a self supporting article. The treatment should also not be in such an amount so as to result in a finished part that is brittle and easily broken during handling for its intended purpose. Typically, the amount of solids from a rigidizing solution (dry weight percent) added to a surface of a die cut sheet material is equal to about 10 percent of the dry weight of the die cut part.

Once the sheet material is treated with a rigidizing solution, the sheet material is formed into the desired shape by preferably, placing the treated sheet material in between inner and outer metal end cone housings, clamping the housings together, placing the assembly into an oven to dry the sheet material, to form the preform

insulating end cone, removing the assembly from the oven, allowing the assembly to cool to room temperature and then removing the preform insulating end cone from the metal housings. Of course, the treated sheet materials may also be formed using any suitable mold having the shape of the desired finished article.

5 Another method of treating at least one of the surfaces of the sheet material used to make the preform insulating end cones of the invention is to apply a shape retaining element in the form of thin layer of metal foil the surface of a sheet material. The metal foil layer can be any metal that can be formed into a three dimensional article for use in a pollution control device. The metal layer may be
10 applied to the surface of the sheet material by means of an adhesive. The metal layer preferably has a thickness of from about 0.0030 inches (0.076 mm) to about 0.0100 inches (0.254 mm). A preferred metal is aluminum and the layer of aluminum is preferably applied to the surface of the sheet material by means of a aluminum tape such as T-49 Foil Tape (from Minnesota Mining and Manufacturing Company, St.
15 Paul, MN.) In use, the metal layer is preferably placed over one or both of the surfaces of the sheet material prior to cutting the material to the desired shape and dimension.

 Another method of treating at least one surface of a sheet material used to make preform insulating end cones of the invention is to apply a shape retaining
20 element in the form of a heat shrinkable film layer to the surface of the sheet material. A heat shrinkable film may be applied over one or both of the entire surfaces of the sheet material and is preferably applied over a portion of the surfaces of the sheet material. Examples of useful heat shrinkable films include polyolefins including polyesters such as SCOTCHPAK™ Type 115 polyester film tape (from Minnesota
25 Mining and Manufacturing Company, St. Paul, MN).

 In use, the heat shrinkable film is applied one or both surfaces of a sheet material using an adhesive or tape or other attachment means and the sheet material is die cut to the desired shape and dimensions. The cut and film covered sheet material is positioned around the outer surface of the inner metal end cone housing
30 and heat is applied to the film until the film shrinks to form a self-supporting end cone. The required thermal energy or heat may be applied by means of a heat gun or a convection oven and the like and is preferably applied by means of a heat gun.

Alternatively, the die cut sheet material is cut to the desired shape and dimensions, is positioned onto the inner metal end cone housing, and a strip or band of heat shrinkable film is wrapped around the edge of the sheet material having the largest circumference, that is, the top or tabbed portion of the end cone and then sufficient heat is applied to shrink the film to form a self-supporting preform end cone. A preferred heat shrinkable film material is polyester and the heat shrinkable film is preferably applied over the top or tabbed portion of the cut sheet material.

Another method of making preform insulating end cones of the invention comprises the steps of providing intumescent or non-intumescent materials that contain a shape retaining element in the form of an organic binder comprising a thermoplastic and/or a thermosetting polymer material, said sheet material cut into the desired shape, forming the cut sheet material into the desired finished three dimensional shape, and then heating the formed intumescent or non-intumescent sheet to a sufficient temperature and for a sufficient time so to melt or partially melt and/or cure the polymeric organic binder and cause it to fuse to form a three dimensional and self-supporting preform insulating end cone. In the case of a thermoplastic polymer material, the finished preform insulating end cone is formed after the formed sheet material is cooled. The cut sheet material can be formed by placing the sheet material into a mold having the desired shape and dimensions and then heating the mold containing the cut sheet material as described above.

The amount of the thermoplastic and /or thermosetting polymer material contained within the intumescent or non-intumescent sheet material should be sufficient to form a self-supporting article from a sheet material. The thermoplastic and/or thermosetting resin contained within the sheet material should not be present in an amount to provide a preform article that would be subject to undesirable cracking or breaking during handling for its intended purpose.

Another method of making preform endcones of the invention comprises the steps of providing an intumescent or a non-intumescent sheet material containing a shape retaining element in the form of an organic binder that comprises an aqueous polymer emulsion, for example, a polymer or elastomer in latex form, the sheet material being cut into the desired shape and dimensions, placing the cut sheet material into a mold having the dimensions to make the desired finished article,

1 saturating the molded sheet material with water, and then heating the sheet material
2 contained within the mold until the water has evaporated to form a finished preform
3 article. Alternatively, the molded sheet material can be saturated by means of
4 applying steam to the sheet material within the mold, and then allowing the sheet
5 material within the mold to dry at room temperature to form the finished preform
6 article. Typical water content of the treated intumescent or non-intumescent sheet
7 material during the forming step ranges from about 5 to about 55 percent by weight
8 of the sheet material.

9 The intumescent or non-intumescent sheet materials used to form the articles
10 of the invention may also contain one or more organic fibers as shape retaining
11 elements in addition to the organic binders described above.

12 In use, the preform insulating end cones of the invention are placed within the
13 inner and outer end cone housings and the housings are welded together to form a
14 conical inlet or outlet for a pollution control device. The conical inlet or outlet is
15 then welded to the metal housing of the pollution control device. The insulating end
16 cones are useful for suppressing noise and vibration in a pollution control device and
17 also for providing thermal insulation from exhaust heat.

Examples

20 Test Methods

Hardness Test

21 The hardness of the treated surfaces of the finished preform end cone
22 insulating liners was determined using a Shore Durometer™ Hardness Tester Type A
23 instrument.

25

Resiliency Test Method

26 This test is used to measure the amount of resiliency of a preform article as a
27 function of retained height of the preform article after a mass is applied.

28 A preform end cone is placed on a level surface with the large diameter
29 opening down (inverted cone). A sheet of rigid cardboard is placed onto the
30 opposite surface. A 20 gram weight is placed on the cardboard and centered over the
31 end cone and the height of the cardboard sheet is recorded as the "Initial Height."

The 20 g weight is removed and 200 g and 50 g weights are placed onto the cardboard as above and the height of the cardboard sheet is recorded as "Final Height." Resiliency is calculated by using the following formula: Resiliency = (final height/initial height) X 100%. Each of the samples tested should have substantially the same dimensions.

Generally, the preform insulating end cones of the invention have a resiliency value of from about 35 to about 97 percent, preferably from about 50 to about 97 percent, and more preferably, about 75 to about 97 percent.

10 Test Method to Determine Thickness and Density Variation

This method is used to determine the variation in thickness and density of formed articles. At least 12 die cut pieces must be removed from each sample. The die cut pieces are taken from the edges and middle portions of each sample. The die is a circular die having a diameter of 11 mm. A pressure of about 13.6 psi (93.6 kPa) is exerted on each die cut piece of each example and then each sample is measured for thickness to the nearest 0.003 cm. These measurements can be performed using a dial gauge available from Federal, Providence, RI. Each die cut piece is weighed to the nearest 0.01g and the weights recorded in grams. Weight per unit area (g/m^2) is calculated by using the following formula: Weight per unit area = (weight (g))/((121 mm² X pi)/4,000,000). The thickness and weight per unit area values are averaged and 3 standard deviations are calculated.

Generally, the preform insulating end cones of the invention have thickness variability (3 standard deviations) of less than 50 percent, preferably less than 30 percent, and more preferably less than 20 percent.

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Example 1

A sheet of intumescent sheet material (INTERAM™ Type 200 mat (3100 g/m^2 available from Minnesota Mining and Manufacturing Company, St. Paul, MN) was die cut using a die cutter (Rotomatic™ II, from Ampak, Inc., Anderson, SC) to form a die cut part similar to that shown in Fig. 2 such that it would conform to the geometry of an outer metal cone housing. The die cut part had general dimensions of 144 mm by 155 mm and weighed about 48.4 g. The part was treated on the entire

surface of one side with a colloidal silica solution (Nalco™ 2327, from Nalco Chemical Company, Naperville, IL) with a paint brush. The coated part was placed into an outer metal cone housing similar to that shown in Fig. 1 (female portion) with the coated surface up. The coated part was pressed into the shape of the outer cone housing with an inner cone housing (male portion). The inner cone housing was removed, the formed part inside the outer cone housing was placed into a forced air laboratory oven (Blue M OV-560A-2, from Blue M Electric Company, Blue Island, IL) and dried for about 1 hour at a temperature of 110°C. After drying, the formed preform was removed from the outer cone housing, allowed to cool, and was weighed. The finished preform had a weight of 52.7 g.

The dried preform insulating material was self supporting and kept its formed shape during handling. The uncoated surface of the preform was soft and compressible and had a measured hardness value of about 25 when measured using the Durometer™ Hardness Tester and method described above. The coated surface of the preform had a measured hardness of about 40. When placing the preform into the outer and inner metal cone housings, the preform remained flexible and conformable and could easily be placed into the housings.

Example C1

The procedure used in Example 1 was repeated to form a finished preform except that the die cut part was saturated with colloidal silica by immersing the part into a container containing a colloidal silica solution. After drying, the coated preform had a weight of 77 g. The finished preform was self supporting and felt very rigid. The measured hardness value of both surfaces ranged from 70 to 80. When fitting the preform inside of the inner and outer housings, one of the tab portions of the part cracked.

Examples 2-3

A sheet of intumescent mat material (INTERAM™ Type 100, 3662 g/m², from Minnesota Mining and Manufacturing Company) and a sheet of non-intumescent mat material (FIBERFRAX™ 550K fiber sheet, from Unifrax, Niagara Falls, NY) were die cut as described in Example 1 to form die cut Examples 2 and 3.

The composition of the intumescent sheet material was about (dry weight percent) 42.5 to about 62.5 percent unexpanded vermiculite, 27 to 45 percent inorganic fiber, 3 to 10 percent latex organic binder. The composition of the non-intumescent sheet material was about 90 percent inorganic fiber and 10 percent latex organic binder.

- 5 The samples were moistened in tap water by immersion under running tap water and then each of the saturated die cut materials were placed in between similar outer and inner end cone housings to those described in Example 1 above. The inner and outer end cone housings were clamped together and then placed in an oven at a temperature of 100°C for about 60 minutes until the water had evaporated. The
- 10 clamped end cone housings containing the die cut materials were removed from the oven, allowed to cool to room temperature, and the formed intumescent and non-intumescent preforms were removed. Both of the intumescent and non-intumescent preform insulating materials were flexible and self supporting and compressible and could be handled without cracking or breaking.

15

Examples 4-5

- Aluminum foil tape, 4 mm thick, (T-49 foil tape, from Minnesota Mining and Manufacturing Company, St. Paul, MN) was laminated to a sample of intumescent sheet material (INTERAM™ Type 100, 3662 g/m², from Minnesota Mining and
- 20 Manufacturing Company) having dimensions of about 35 cm by 35 cm such that an entire surface of the intumescent sheet material was covered. The foil covered sheet material was then die cut as in Example 2. The foil coated die cut part was then formed over the outside surface of an inner metal cone housing with the foil side adjacent to the outside surface of the inner end cone housing. The outside end cone
- 25 casing was then placed over the outside of the insulating material and positioned properly into a finished end cone. The outer end cone housing was removed, and the formed preform was removed. The formed foil coated preform of Example 4 was flexible and self supporting.

- The procedure of Example 4 was repeated except that both sides of the
- 30 intumescent sheet material were covered with the foil tape to form the preform of Example 5. The preform of Example 5 was flexible and self supporting.

Example 6

An intumescent sheet material was die cut as described in Example 2. The die cut material was then formed over the inner end cone housing of Example 2 and a heat shrinkable polyester film, SCOTCHPAK™ Type 115 tape, was wrapped around the top or open edge of the die cut intumescent material such that it extended about 20 mm past the lip or edge of the die cut material. The heat shrinkable film was about 33 mm wide and about 300 mm in length. Heat was applied to the film by means of a 1440 watt heat gun for about 30 seconds until the wrap shrunk around the die cut material. The formed preform was removed from the inner end cone housing and was flexible and self supporting. An advantage of this method of forming a preform end cone insulating material is that a relatively small amount of the shrink-wrap film is required to form the preform of the invention.

Example 7

A die cut intumescent sheet material as described in Example 2 was coated on one side with the rigidizing solution described below. The rigidizing solution was applied to the die cut material using a small paintbrush until the entire surface of the material appeared wet. The rigidizing solution was a 5:1 magnesium phosphate cement in deionized water (ZYPT™ RS-1000 cement, from ZYP Coatings Inc., Oak Ridge, TN). The coated sample was placed between inner and outer end cone housings as described in Example 2. The clamped end cone housing containing the coated sample was placed in a 100C oven for about 60 minutes until the coating dried to form the preform end cone article. The resulting preform end cone was flexible and self supporting and could be handled without undesirable cracking or breaking.

Example 8

A sheet of intumescent sheet material (INTERAM™ Type 100, 3662 g/m², from Minnesota Mining and Manufacturing Company) was laminated on one surface with a polyester film tape (3M Tape # 356) and then die cut into the shape as shown in Figure 4. The ends were brought together such that the cut sheet material was in the shape of a cone and then the ends were taped together with a piece of the

polyester film tape to form the finished preform insulating end cone shown in Figure 5.

Examples 9-12 and Comparative Examples C2-C4

5 Examples 8-13, described below, were tested for resiliency using the Resiliency Test Method described above.

 Example 9 was the preform of Example 1.

 Example 10 was the preform of Example 2.

 Example 11 was the preform of Example 4.

10 Example 12 was the preform of Example 6.

 Example 13 was the preform of Example 8.

 Comparative Examples C2, C3, and C4 were also tested using the above method.

 C2 was the comparative preform C1.

15 C3 was a slush molded end cone insulating liner that was made using a mold having the same shape as the mold used in Example 1. The composition of C3 was about 7.35 dry weight percent of starch binder and about 92.65 dry weight percent of refractory ceramic fiber.

 C4 was a slush molded insulating liner made as described in C3 above having
20 a composition of about 14 dry weight percent starch binder and 86 percent by weight shredded intumescent sheet material (INTERAM™ X-D mounting material, from Minnesota Mining and Manufacturing), the shredded intumescent sheet material having a dry weight composition of about 45-62.5% unexpanded vermiculite, 27.5 -
25 45% ceramic fiber, and 3-10% organic binder. The slush molded end cone liners were made by making dilute aqueous slurries, placing a permeable mold into each of the slurries and removing the water using gravity and/or vacuum and then drying the formed end cone liners on the mold. The results are shown in Table 1 below.

Table 1

Example	Resiliency (%)
9	97
10	79
11	49
12	97
13	94
C2	99
C3	100
C4	100

The results show that the preform insulating end cones of the invention are more compressible than preform end cones having similar compositions that are saturated with a rigidizing solution and that are slush molded. Thus, the preforms of the invention are easier to handle in a manufacturing process and are less prone to breaking and splitting than saturated or slush molded end cone liners.

Example 14 and Comparative Examples C5 and C6

The intumescent sheet material used to make the preform insulating end cone of Example 10 (Example 14 below) and comparative examples C3 (C5 below) and C4 (C6 below) were tested for thickness and density variability using the method described above. The results are shown in Table 2 below.

15

Table 2

N=12	Comparative Example 5	Comparative Example 6	Example 14
Average Thickness (in.)	0.26	.338	0.206
3 Std. Dev.	0.05	.217	0.02
+ or - 3 Std. Dev.	21%	64%	8%
Average Weight (g)	0.21	0.42	0.33
3 Std. Dev.	0.02	0.33	0.06
+ or - 3 Std. Dev.	9%	79%	17%
Average Weight Per Area (g/M ²)	2211	4404	3501
3 Std. Dev.	190	3478	589
+ or - 3 Std. Dev.	9%	79%	17%

5 The results show that the intumescent preform insulating end cone of the invention has a more uniform thickness than does slush molded end cone liners of the same dimensions and a more uniform density (weight per unit area) than a slush molded intumescent end cone liner. Additionally, the preform insulating end cone of the invention maintains the resiliency and compressibility of the intumescent sheet material whereas the slush molded end cone liners are relatively hard and brittle.

10

What is claimed is:

1. A preform insulating end cone suitable for forming the end cone of a pollution control device, said preform comprising:
 - 5 a cone shaped intumescent sheet material having a plurality of slits enabling said sheet material to be cone shaped; and
 - a shape retaining element in intimate contact with said intumescent sheet material, said shape retaining element enabling said intumescent sheet material to maintain a cone shape.
- 10 2. The preform insulating end cone of claim 1 wherein said shape retaining element is an organic binder.
3. The preform insulating end cone of claim 2 wherein the organic
15 binder is a polymer emulsion.
4. The preform insulating end cone of claim 1 wherein said shape retaining element is a metal foil.
- 20 5. The preform of claim 1 wherein said shape retaining element is a heat shrinkable film.
6. The preform of claim 2 wherein the organic binder is a thermoplastic material.
- 25 7. The preform insulating end cone of claim 2 wherein the organic binder comprises a thermosetting material.
8. The preform insulating end cone of claim 1 wherein said shape
30 retaining element is a rigidizing solution.

9. The preform insulating end cone of claim 8 wherein the rigidizing solution is selected from the group consisting of aqueous colloidal silica, aqueous colloidal alumina, monoaluminum phosphate, magnesium phosphate, vermiculite emulsions, and clay emulsions.

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10. A preform insulating end cone suitable for forming the end cone of a pollution control device, said preform comprising:

a cone shaped intumescent sheet material having a first end and a second end; and

10

a shape retaining element in intimate contact with said intumescent sheet material, said shape retaining element enabling said intumescent sheet material to maintain a cone shape.

11. The preform insulating end cone of claim 10 wherein said shape retaining element is a tape joining said first end and said second end together.

15

12. The preform insulating end cone of claim 11 wherein said shape retaining element further comprises a thermoplastic film laminated to a surface of said sheet material wherein said tape is adhered to said thermoplastic film.

20

13. A pollution control device comprising:

(a) a metallic housing;

(b) a monolithic catalytic element;

(c) an inlet and an outlet metallic end cone assembly for attaching

25 exhaust pipes to the metallic housing, each end cone assembly comprising an inner end cone housing and an outer end cone housing; and

(d) a preform insulating end cone of any one of claims 1-12 disposed between the inner and outer end cone housings.

30 14. A method of making the preform insulating end cone of claim 1 or claim 10 for use in a pollution control device comprising the steps of:

(a) providing an intumescent or a non-intumescent insulating material in the form of a sheet having first and second major surfaces and having the desired dimensions for the finished preform insulating end cone, said insulating material containing an organic binder comprising a polymeric emulsion;

5 (b) treating said insulating material with water or steam;

(c) forming said treated insulating material into the desired shape for the finished preform insulating end cone; and

(d) drying said formed insulating material to form a finished preform insulating end cone.

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15. The method of claim 14 wherein said sheet material is intumescent.

16. The method of claim 15 wherein said intumescent sheet material comprises from about 20 to 65 percent by dry weight of an intumescent material,
15 from about 10 percent to 50 percent by dry weight of inorganic fibrous material, from about 3 to 25 percent by dry weight of organic binder, and up to about 40 percent by dry weight of inorganic filler.

17. The method of claim 14 further comprising the step of forming said
20 treated insulating material into the desired shape by placing said treated insulating material in a mold having the dimensions of an end cone assembly of a pollution control device.

18. A method of making the preform insulating end cone of claim 1 or
25 claim 10 for use in a pollution control device comprising the steps of:

(a) providing an intumescent or a non-intumescent insulating material in the form of a sheet having first and second major surfaces and having the desired dimensions for the finished preform insulating end cone;

(b) treating a surface of said insulating material with a rigidizing
30 solution selected from the group consisting of aqueous colloidal silica, aqueous colloidal alumina, monoaluminum phosphate, magnesium phosphate, vermiculite emulsions, and clay emulsions;

(c) forming said treated insulating material into the desired shape for the finished preform insulating end cone; and

(d) drying said formed insulating material to form a finished preform insulating end cone.

5

19. A method of making the preform insulating end cone of claim 1 or claim 10 for use in a pollution control device comprising the steps of:

(a) providing an intumescent or a non-intumescent insulating material in the form of a sheet having first and second major surfaces and having the desired dimensions for the finished preform insulating end cone;

(b) treating a surface of said insulating material by applying a metal foil over a surface of said insulating material; and

(c) forming said treated insulating material into the desired shape to form a finished preform insulating end cone.

15

20. A method of making the preform insulating end cone of claim 1 or claim 10 for use in a pollution control device comprising the steps of:

(a) providing an intumescent or a non-intumescent insulating material in the form of a sheet having first and second major surfaces and having the desired dimensions for the finished preform insulating end cone;

(b) forming said insulating material into the desired shape for the finished preform insulating end cone;

(c) treating a surface of said insulating material by applying a heat shrinkable film over a surface of said insulating material; and

(d) heating the heat shrinkable film to a sufficient temperature so to cause the film to shrink to form the finished preform insulating end cone.

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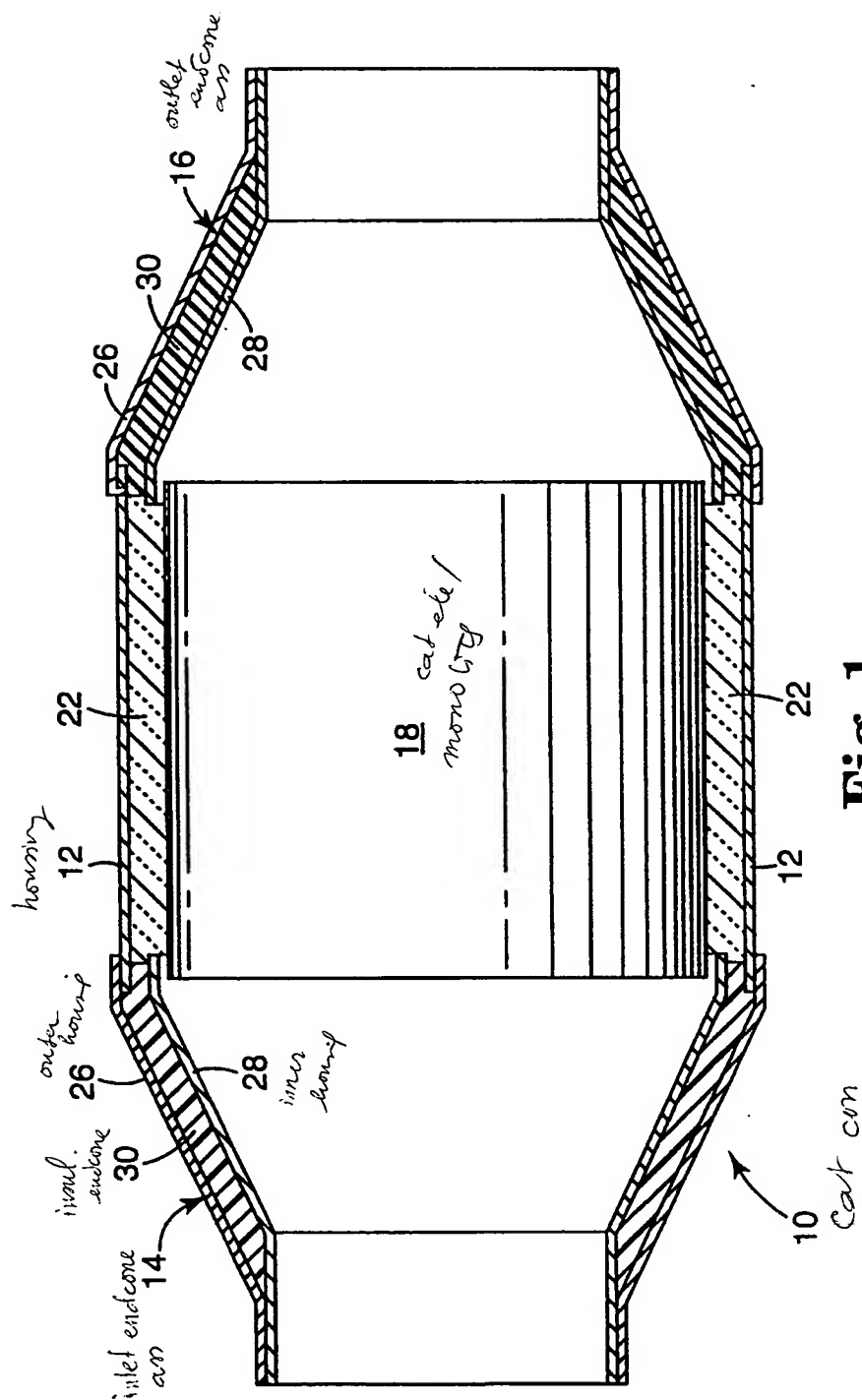
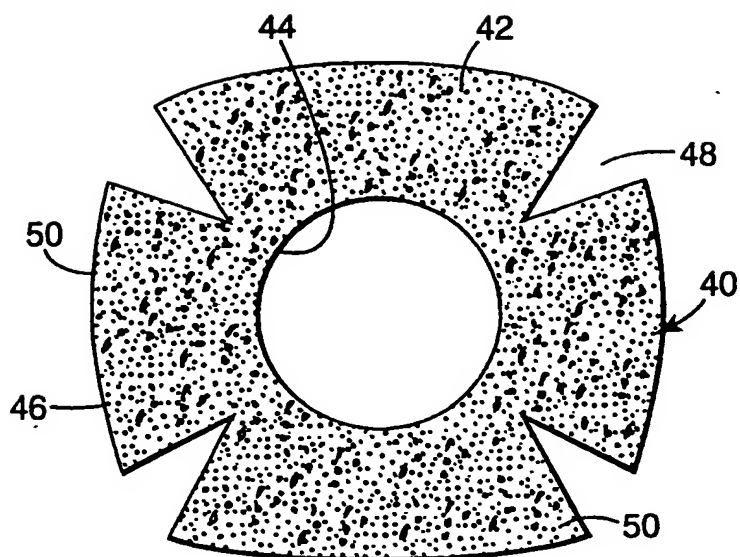
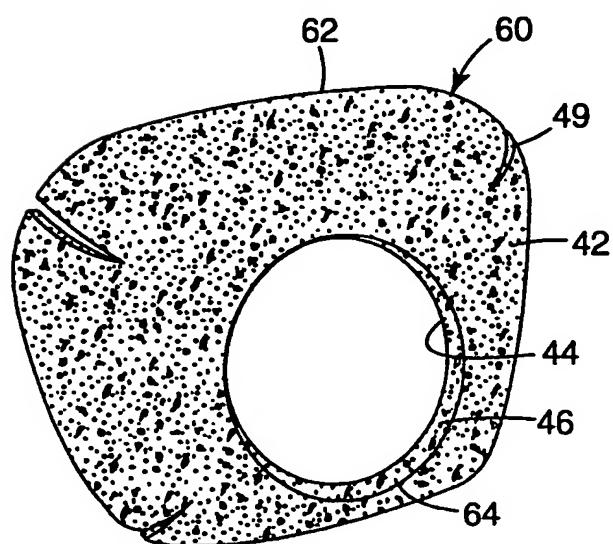


Fig. 1

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**Fig. 2****Fig. 3**

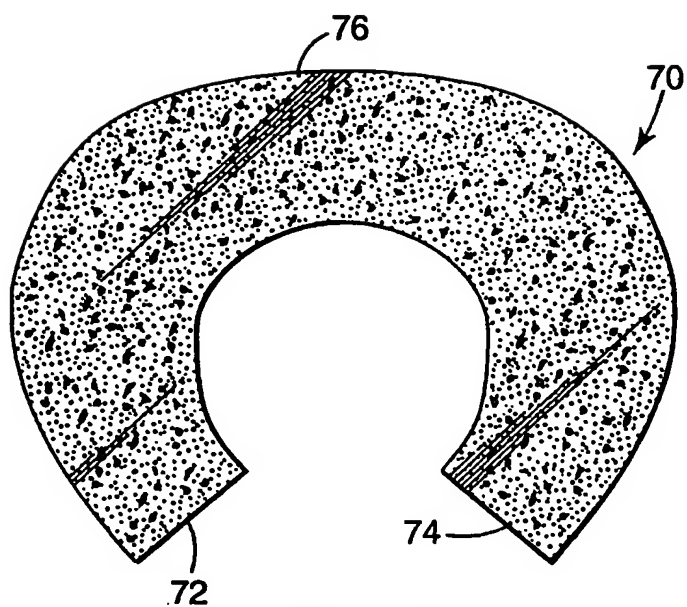


Fig. 4

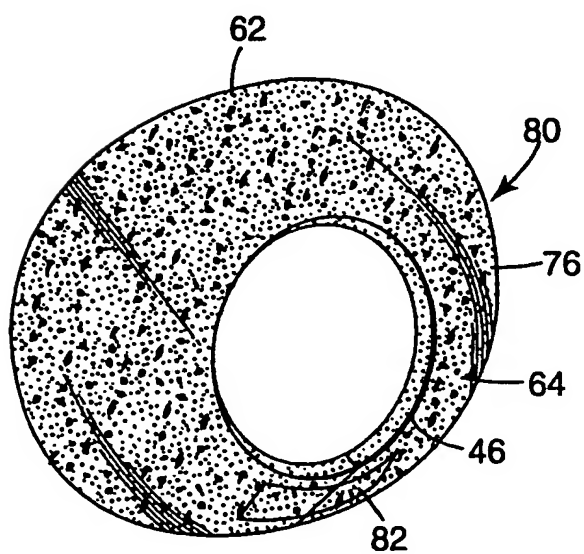


Fig. 5

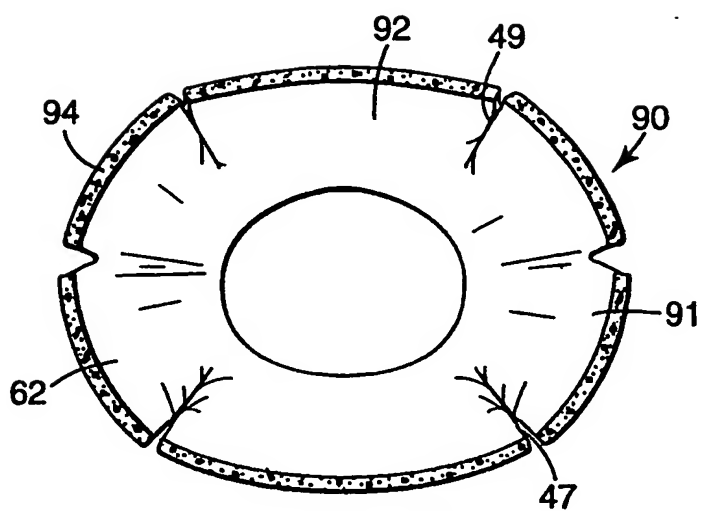


Fig. 6

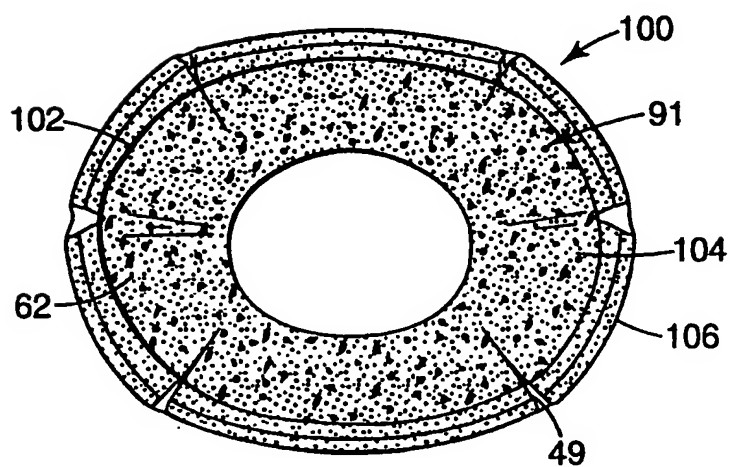


Fig. 7

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/15864

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 F01N7/14 F01N3/28 F01N3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 F01N C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 413 998 A (LEISTRITZ AG) 27 February 1991 see the whole document	1,10,13
A	US 4 999 168 A (TEN EYCK JOHN D) 12 March 1991 see column 4, line 24 - column 5, line 64; figures 1-3	1,10
A	DE 25 49 255 A (VOLKSWAGENWERK AG) 5 May 1977	
A	US 4 378 046 A (KLINGER WILHELM) 29 March 1983	
A	DE 38 35 841 A (EBERSPAECHER J) 26 April 1990	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/15864

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0413998 A	27-02-91	DE 3927895 C DE 59003214 D ES 2045681 T	13-09-90 02-12-93 16-01-94
US 4999168 A	12-03-91	AU 631634 B AU 5454290 A CA 2015717 A EP 0396331 A JP 3007333 A	03-12-92 01-11-90 01-11-90 07-11-90 14-01-91
DE 2549255 A	05-05-77	NONE	
US 4378046 A	29-03-83	DE 2907767 A	11-09-80
DE 3835841 A	26-04-90	NONE	